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ON THIS 13th DAY OF June, 2001.

BY

*Richard M. Beck*

1998/G 021 (5587\*311)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

JENS EHLERS ET AL :

SERIAL NO: 09/787,875 :

ART UNIT:

FILED: MARCH 22, 2001 :

EXAMINER:

FOR: PROCESS FOR PREPARING A  
POLYMER :

Assistant Commissioner for Patents  
Washington, D.C. 20231

TRANSMITTAL OF MISSING PARTS

Sir:

Please find the enclosed papers:

1) Original Declaration/Power of Attorney form executed by inventors: Jens Ehlers, Stanislaw Haftka and Louis Wang.

2) The undersigned's check for \$130.00 to cover the surcharge for missing parts.

3) A copy of the Notice to File Missing Parts of Non-provisional application.

The Commissioner is authorized to debit any deficiency, or credit any overpayment,  
of the above-mentioned fees to our Deposit Account No. 03-2775.

06/21/2001 ATRM

00000061 09787875

01 FC:154

130.00 BP

Respectfully submitted,

CONNOLLY, BOVE, LODGE & HUTZ, LLP

By

*Richard M. Beck*

Richard M. Beck

Reg. No. 22,580

Tel. (302) 658-9141

RMB/alh/:.ODMA\MHODMA\CB;148229;1

09/787875

Atty. Docket #: 1998/G-021

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**INTERNATIONAL APPL. NO.:** PCT/EP99/07085 :

**INTERNATIONAL FILING DATE:** -09/23/1999- :

**APPLICANT:** JENS EHLERS ET AL :

**SERIAL NO.:** : **ART UNIT:**

**FILED:** -HEREWITH- : **EXAMINER:**

**FOR:** "PROCESS FOR PREPARING  
A  
POLYMER" :

Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

"Express Mail" No.: EE617838466

Date: - MARCH 22, 2001 -

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231

- Amy L. Hamm -  
(Typed or printed name of mailing paper or fee)

*Amy L. Hamm*  
(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS  
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371  
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

09787875-01901

09/787875

- 09787875-071901
1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
  3. ☒ This is an express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay.
  4. ☒ A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
  5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)[2]) --
    - a. ☒ is transmitted herewith (required when not transmitted by International Bureau).
    - b. ☐ has been transmitted by the International Bureau. See WIPO Publication WO 00/18809.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☒ A (verified) translation of the International Application into the English language is enclosed.
  7. ☒ Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)[3])
    - a. ☒ are transmitted herewith (required if not transmitted by the International Bureau).
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☐ have not been made and will not be made.
    - e. ☐ will be submitted with the appropriate surcharge.
  8. ☐ A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371(c)[3]) is enclosed or will be submitted with the appropriate surcharge.

09/787875  
1998/G-021

International Application No. PCT/EP99/07085

9. ☒ An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371(c)[4]) will follow.  
☐ and is attached to the translation of (or a copy of) the International Application.  
☐ and is attached to the substitute specification.

10. ☐ A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371(c)[5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.  
12. ☒ An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.  
13. ☒ A FIRST preliminary amendment is enclosed.  
A SECOND or SUBSEQUENT preliminary amendment is enclosed.  
14. ☐ A substitute specification (including claims, abstract, drawing) is enclosed.  
15. ☐ A change of power of attorney and/or address letter is enclosed.  
16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of-

☐ 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☒ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

09/787875

International Application No. PCT/EP99/07085

1998/G-021

- ☒ Receiving Office: EPO
- ☒ IPEA (if filing under 37 CFR 1.495): EPO
- ☒ Priority Claim(s) (35 USC §§ 119, 365):  
German Appln. 198 43 858.3 filed -September 25, 1998-
- ☒ A copy of the International Search Report is

☐ enclosed.

☒ attached to the copy of the International  
 Application.

- ☒ A copy of the Receiving Office Request Form is enclosed.

- ☒ Form PCT/IB7308 - (1) sheet
- ☒ Amended Sheet, Page 7, English
- ☒ Amended Sheet, Page 7, German
- ☒ Amended Sheets, Pages 1-9, English
- ☒ Amended Sheets, Pages 1-10, German

The fee calculation is set forth on the next page of this Transmittal Letter.

09/787875

## FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 860.00

Total Number of claims in  
excess of (20) times \$18..... -0-

Number of independent claims  
in excess of (3) times \$80 ..... -0-

Fee for multiple dependent  
claims \$270..... -0-

TOTAL FILING FEE... \$ 860.00  
=====

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By Richard M. Beck  
Richard M. Beck  
Reg. No. 22,580  
CONNOLLY BOVE LODGE & HUTZ LLP  
1220 Market Street  
P.O. Box 2207  
Wilmington, Delaware 19899  
Tel. (302) 658-9141

RMB/alh (5587\*311)

Enclosures

F:\docs\fori\40975 = F:\docs\patn\56657.doc

1998/G-021

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

..... : INT'L APPLN: PCT/EP99/07085

JENS EHLERS ET AL

SERIAL NO: : ART UNIT:

FILED: -HEREWITH- : EXAMINER:

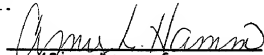
FOR: "PROCESS FOR :  
PREPARING A :  
POLYMER" :  
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.....  
Commissioner  
for Patents  
Washington, D.C. 20231

"Express Mail" No.: EE617838466 Date: - MARCH 22, 2001 -

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Box PCT, Commissioner for Patents, Washington, D.C. 20231.

- Amy L. Hamm -  
(Typed or printed name) of  
person mailing paper or fee)

  
(Signature of person  
mailing paper or fee)

PRELIMINARY AMENDMENT

Sir:

Prior to any action on the merits of the accompanying new patent application, kindly amend the application as follows:

In the Claims:

Attached please find a separate clean version of amended claims 3-6 and 9-11, followed by a 'marked-up' version:

1998/G-021  
Clean Copy Claims

3. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1, wherein the melt flow index (MFR is from 1.4 g/10 min to 5 g/10 min, 190/15)  
the molecular weight is from 4 to 8,  
distribution  $M_w/M_n$   
the bulk density is from 0.13 g/cc to 0.3 g/cc and  
the particle size is from 60  $\mu\text{m}$  to 180  $\mu\text{m}$ .
4. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1, wherein  
the melt flow index (MFR is from 1.4 g/10 min to 3 g/10 min, 190/15)  
the molecular weight is from 4 to 8,  
distribution  $M_w/M_n$   
the bulk density is from 0.15 g/cc to 0.28 g/cc and  
the particle size is from 60  $\mu\text{m}$  to 160  $\mu\text{m}$ .
5. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1, wherein the polymerization is carried out at a temperature of from 30°C to 130°C and a pressure of from 0.05 MPa to 4 MPa.
6. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1, wherein the polymerization is carried out at a temperature of from 50°C to 90°C.



1998/G-021  
Clean Copy Claims

9. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 7, wherein the reaction of the Ti(IV) compound with the organic aluminum compound is carried out in a saturated hydrocarbon or a mixture of saturated hydrocarbons at a temperature of from  $-40^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ .
10. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 7, wherein the concentrations of the reactants in the starting solutions are from 0.1 mol to 9.1 mol of Ti(IV) compound/l of solvent and 0.01 mol to 1 mol of Al compound/l.
11. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 7, wherein the reaction of the components is carried out by adding the Ti(IV) component to the Al component over a period of from 0.1 minute to 60 minutes.

R E M A R K S

Claims 3-6 and 9-11 have been amended to refer to only one preceding claim. Each of the dependent claims, as amended, now depends on only one preceding claim. Therefore no additional fee is required for multiple dependence.

Prompt, favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By Richard M. Beck  
Richard M. Beck, Reg. No. 22,580  
P.O. Box 2207  
Wilmington, Delaware 19899  
(302) 888-6235  
Attorney for Applicants

RMB/alh  
(5587\*311)

Marked-up Version  
follows

3. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1 [or 2], wherein the melt flow index (MFR) is from 1.4 g/10 min to 5 g/10 min, 190/15)  
the molecular weight is from 4 to 8,  
distribution  $M_w/M_n$   
the bulk density is from 0.13 g/cc to 0.3 g/cc and  
the particle size is from 60  $\mu\text{m}$  to 180  $\mu\text{m}$ .
4. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in [one or more of] claim[s] 1 [to 3], wherein  
the melt flow index (MFR) is from 1.4 g/10 min to 3 g/10 min, 190/15)  
the molecular weight is from 4 to 8,  
distribution  $M_w/M_n$   
the bulk density is from 0.15 g/cc to 0.28 g/cc and  
the particle size is from 60  $\mu\text{m}$  to 160  $\mu\text{m}$ .
5. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in [one or more of] claim[s] 1 [to 4], wherein the polymerization is carried out at a temperature of from 30°C to 130°C and a pressure of from 0.05 MPa to 4 MPa.
6. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in [one or more of] claim[s] 1 [to 5], wherein the polymerization is carried out at a temperature of from 50°C to 90°C.

1998/G-021  
MARKED-UP VERSION

9. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 7 ~~for 8~~, wherein the reaction of the Ti(IV) compound with the organic aluminum compound is carried out in a saturated hydrocarbon or a mixture of saturated hydrocarbons at a temperature of from  $-40^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ .
10. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in ~~one or more of] claim~~s] 7 [to 9, wherein the concentrations of the reactants in the starting solutions are from 0.1 mol to 9.1 mol of Ti(IV) compound/l of solvent and 0.01 mol to 1 mol of Al compound/l.
11. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in ~~[one or more of] claim~~s] 7 [to 10, wherein the reaction of the components is carried out by adding the Ti(IV) component to the Al component over a period of from 0.1 minute to 60 minutes.

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PCT/EP99/07085

WO 00/18809

## Description

## Process for preparing a polymer

- 5 The present invention relates to a process for preparing a catalyst, a novel polymer and a process for preparing the polymer.

10 In processing of polyethylene, the polyethylene is usually melted and shaped to form a compact molding. From an economic point of view, the use of a polymer which is as compact as possible is always desirable. This objective becomes particularly clear in the preparation and use of ultrahigh molecular weight polyethylene. This is described in the prior art in JP-A-07041514, JP-A-06179720, EP-A-574153, JP-A-05070519.

- 15 Fillers are predominantly distributed homogeneously in the melt of the polymer. If this is impossible from a processing point of view, the use of polymer having an irregular structure is a possibility. The bulk density of the polymer can be employed as an easy-to-use physical measure of the particle and powder morphology. Thus, JP-A-519120423 describes the use of graphite-filled UHMWPE. The use of UHMWPE having a bulk density of less than 0.25 g/ccm is advantageous here.
- 20

- In addition, the processing of UHMWPE under reduced pressure to form porous semifinished and finished parts is known. For use as filter elements,
- 25 a low pressure drop is necessary. Here too, an irregular structure of the sintered UHMWPE material is very helpful; cf. JP-A-09003236, JP-A-09001633.

- 30 In the production of filter elements, both requirements apply at the same time. EP-A-0 554 223 discloses a process for producing a filter unit. The morphology and low bulk density of the binder and the activated carbon are matched to one another. The high viscosity of the binder results in a lower strength of the resulting filter unit.

- 35 US-A-4,753,728 discloses an activated carbon filter block comprising activated carbon particles which are bound by a polymer to form a filter block. The polymer has a melt flow index of less than about 1 gram per 10 minutes, determined in accordance with ASTM D 1238 at 190°C and a

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loading of 15 kilograms. The polymer becomes sticky at elevated temperature. The polymer does not become sufficiently liquid to wet the activated carbon particles to a significant extent. A commercially available polymer GUR<sup>®</sup> 212 which has a melt flow index of < 0.1 gram per 10 minutes, determined in accordance with ASTM D 1238 at 190°C and a loading of 15 kilograms, and is an ultrahigh molecular weight polyethylene is disclosed.

EP-A-0 792 673 discloses a binder for producing filters by the extrusion technique. The binder has very high flow and an inhomogeneous distribution. The inhomogeneous distribution in the mixture leads to a fragile product. In addition, it comes to the surface of the activated carbon through the binder. The result is a decrease in the filter capacity.

Apart from the molar mass and the morphology, the particle size of the polymer also has to be matched to the filler to make homogeneous mixing possible and to reduce demixing during processing of the pulverulent mixtures.

The previously known processes for preparing polyethylene make it possible to influence the external shape of the polymer particles only within very narrow limits. The mean catalyst particle size is usually determined during the preparation of the catalyst. It is known that the catalyst particle size can be influenced in a targeted way by shearing during and after production of the solid catalyst particle by chemical reaction of the individual components. The particle size usually decreases at higher shear. At a circumferential velocity of the stirrer fixed by engineering circumstances, the shear can be controlled by varying the solvent viscosity. If, in addition, the solvent is predetermined, its viscosity can be influenced by means of the temperature. As the temperature decreases, the shear generally increases owing to the higher viscosity of the solvent. This results in catalysts having a low particle size. Thus, the catalyst described in EP-A-0645403 is prepared at a low temperature in order to obtain a finely particulate catalyst. The use of higher viscosity solvents in the preparation of the catalyst also leads to an analogous result.

It is an object of the present invention to provide an economical and environmentally friendly process for preparing a homopolymer and/or copolymer having an irregular particle structure.

- 5 This object is achieved by a process for preparing a homopolymer and/or copolymer having an irregular particle structure, which comprises polymerizing the monomers in the presence of a mixed catalyst comprising a titanium component and an organic aluminum compound and the presence of a molar mass regulator.

10

The process of the invention preferably gives a polyethylene having a viscometrically measured molar mass of  $1.5 - 4.1 \times 10^5$  g/mol (M by the Margolies method =  $5.37 \times 10^4$  [IV]<sup>1.49</sup>), a bulk density of less than 0.4 g/ccm, in particular from 0.05 g/ccm to 0.4 g/ccm, and a mean particle size of 5 – 300 µm and a molar mass distribution  $M_w/M_n$  of 3 – 30.

15

The process of the invention makes it possible to prepare preferably pulverulent polyethylene having particle sizes which can be varied. The molar mass of the polymer should be set so that a material having a

20 measurable flow is obtained. At the same time, a narrow molar mass distribution ensures that the pores of the activated carbon are not blocked during sintering in filter production. Furthermore, sufficient powder flow should ensure good drying and conveying behavior.

25

In addition, variation of the polymer morphology is made possible. This can be achieved by means of the polymerization temperature selected or else by means of the ethylene partial pressure. Both a higher temperature and a higher ethylene partial pressure in the polymerization result in an increase in the bulk density.

30

The titanium component used according to the invention is obtained in a single-vessel reaction. The diluted Ti(IV) compound is reacted with the diluted aluminum compound at from -40°C to 100°C in a molar ratio of from 1:0.01 to 1:4 for from 0.5 minute to 60 minutes.

35

According to the invention, the particle size of the catalyst is determined by the activation temperature of the catalyst. This can influence the particle

size of the polymer, which correlates with the particle size of the catalyst solid because of the replication behavior due to the multigrain behavior.

5 The reaction of the Ti(IV) compound with the organic aluminum compound is carried out in a pure saturated hydrocarbon or a mixture of saturated hydrocarbons at temperatures of from  $-40^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , preferably from  $-20^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ , particularly preferably from  $0^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ . The concentrations of the reactants in the starting solutions are from 0.1 mol to 9.1 mol of Ti(IV) compound/l of solvent and from 0.01 mol to 1 mol of Al compound/l, 10 in particular from 0.2 mol to 5 mol of Ti(IV) compound and from 0.02 mol to 0.2 mol of Al compound.

To react the components, the Ti(IV) component is added to the Al component. The addition time is from 0.1 minute to 60 minutes, preferably 15 from 1 minute to 30 minutes. Depending on the temperature, the reaction is complete after from 1 minute to 600 minutes. Cerimetrically, the Ti(III) yield is at least 95%.

20 The polymerization is carried out in suspension in one or more stages, continuously or batchwise. The polymerization temperature is from  $30^{\circ}\text{C}$  to  $130^{\circ}\text{C}$ , preferably from  $50^{\circ}\text{C}$  to  $90^{\circ}\text{C}$ . The ethylene partial pressure is set in accordance with the bulk density required of the polymer. It is less than 4 MPa, preferably from 0.02 MPa to 2 MPa, particularly preferably from 0.04 MPa to 1 Mpa. As is customary in Ziegler-Natta polymerizations, an 25 organoaluminum compound is used as cocatalyst. The aluminum component is added to the suspension medium in a ratio to the Ti component of Al:Ti = 1:1 - 30:1. The preferred Al:Ti ratio is in the range from 2:1 to 20:1.

30 The reaction medium for the polymerization is, as is customary in Ziegler-Natta polymerizations, an inert solvent such as butane, pentane, hexane, cyclohexane, nonane, decane or their higher homologues and isomers as pure substances or mixtures. The solvent is freed of catalyst poisons such as oxygen, moisture or sulfur compounds before use.

35 The molar masses of the polymers can be adjusted in a known manner by introduction of appropriate components. Preference is given to using



hydrogen. The ratio of ethylene partial pressure to hydrogen partial pressure is from 0.5:1 to 10:1, preferably from 2:1 to 8:1.

5 Addition of 1-olefins makes it possible, as is known, to obtain corresponding copolymers in addition to ethylene homopolymers.

10 The polymer is separated from the suspension medium under inert gas and dried in a fluidized bed. When using high-boiling hydrocarbons, the reaction product is subjected beforehand to treatment with steam.

The suspension medium is returned directly to the polymerization reactor.

15 Stabilizing additives such as the customary salts of long-chain fatty acids, e.g. calcium, zinc or magnesium stearate, can be added to the polymer.

To describe the polymers, the following values are reported:

20 mean particle diameter ( $d_{50}$ ): determined by laser light scattering using the particle size analyzer Helos-Rhodos measurement and data processing system from Sympatec GmbH, optical concentration = 4-7%,

bulk density (BD): determined in accordance with DIN 53 466,

25 melt flow index (MFR): the melt flow index 190/15 was determined in accordance with ISO 1133; 0.2% of ionol were added as stabilizer,

30 viscosity number (VN): determined in accordance with ISO 1628-3 in decalin at a concentration of 0.1 g/dl; to calculate the molar mass, the limiting viscosity (IV) is calculated therefrom using the Martin equation,

B value: this value gives, as dimensionless parameter, information about the particle size of the catalyst. On the basis of the replication effect, the following relationship applies:  $\log(\text{catalyst yield}) = 3 \times \log(d_{50}) - B$ . The smaller the B value, the finer the mean particle diameter of the catalyst.

35 The invention is illustrated by the examples:

Examples

### Preparation of catalyst

13 mol of isoprenylaluminum (IPRA) and 252 l of Exxsol were placed under a protective gas blanket in a 600 l vessel. At an initial temperature of 8°C - 13°C, a solution of titanium tetrachloride in Exxsol<sup>®</sup> D30 (concentration: 3000 mmol/l) was added while stirring, so that a ratio of Ti:IPRA of 1:0.78 was established in the reaction mixture. The addition time was 120 sec - 140 sec. The reaction proceeded exothermically and spontaneously. The temperature rose quickly by 5°C over a period of 4 minutes. The mixture was stirred while cooling for 2 hours to allow further reaction to occur. After 15 hours, the upper phase was decanted off. The solid was admixed with 200 l of Exxsol<sup>®</sup> D30 and 0.7 mol of IPRA, and then used for polymerization.

### Polymerization

The polymerization was carried out in one stage in a continuously operated plant with recirculation of the suspension medium. The suspension medium used was a mixture of saturated hydrocarbons having a boiling point range of 140°C - 170°C (Exxsol<sup>®</sup> D30) which had previously been purified over molecular sieves and aluminum oxide. The polymerization was carried out in a 40 l reactor at a reaction temperature of 70°C - 82°C and an ethylene partial pressure of from 0.16 MPa to 0.27 MPa.

On the basis of experience, the bulk density of the polymer increases by about 0.02 - 0.05 g/l on scale-up.

Examples 5 and 6 were carried out like Examples 1 to 4. In Examples 5 and [lacuna], the amount of catalyst used was reduced from 0.95 mmol of Ti/kg of PE to half this quantity. To be able to achieve the required product properties, both the reaction temperature and the ethylene partial pressure were increased compared to Examples 1 to 4.

The parameters and measurement results are shown in the table below.

Table

Activation temp. of the catalyst	Polymer -ization temp.	p(C <sub>2</sub> H <sub>4</sub> )	C <sub>2</sub> H <sub>4</sub> / H <sub>2</sub>	MFR 190/15	BD	d(50)	B value	Ex.
[°C]	[°C]	[bar]		[g/10min]	[g/l]	[μm]		
9	70	2.20	2.04	1.6	163	97	3.52	1
10	70	1.65	1.92	1.9	161	145	3.47	2
11	70	1.65	2.04	1.6	171	97	2.94	3
12	70	1.68	2.23	1.8	187	84	2.80	4
10	82	2.7	n.d.	1.4	190	172	3.41	5
13	80	2.4	n.d.	1.4	230	85	2.42	6

007878.07190

## Claims

1. A process for preparing a homopolymer and/or copolymer having an irregular particle structure and
 

a melt flow index (MFR 190/15)	of from 1.3 g/10 min to 10 g/10 min,
a molecular weight distribution $M_w/M_n$	of from 3 to 30,
a bulk density	of from 0.05 g/cc to 0.4 g/cc and
a particle size	of from 5 $\mu\text{m}$ to 300 $\mu\text{m}$ ,
- 5 which comprises polymerizing the monomers in the presence of a mixed catalyst comprising a titanium component and an organic aluminum compound and the presence of a molar mass regulator.
- 10 2. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1, wherein
 

the melt flow index (MFR 190/15)	is from 1.3 g/10 min to 10 g/10 min,
the molecular weight distribution $M_w/M_n$	is from 3 to 10,
the bulk density	is from 0.1 g/cc to 0.4 g/cc and
the particle size	is from 20 $\mu\text{m}$ to 200 $\mu\text{m}$ .
3. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1 or 2, wherein
 

the melt flow index (MFR 190/15)	is from 1.4 g/10 min to 5 g/10 min,
the molecular weight distribution $M_w/M_n$	is from 4 to 8,
the bulk density	is from 0.13 g/cc to 0.3 g/cc and
the particle size	is from 60 $\mu\text{m}$ to 180 $\mu\text{m}$ .
- 15 4. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 3, wherein
 

the melt flow index (MFR 190/15)	is from 1.4 g/10 min to 3 g/10 min,
the molecular weight	is from 4 to 8,

distribution  $M_w/M_n$

the bulk density

is from 0.15 g/cc to 0.28 g/cc and

the particle size

is from 60  $\mu\text{m}$  to 160  $\mu\text{m}$ .

5. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 4, wherein the polymerization is carried out at a temperature of from 30°C to 130°C and a pressure of from 0.05 MPa to 4 MPa.
6. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 5, wherein the polymerization is carried out at a temperature of from 50°C to 90°C.
7. A process for preparing a catalyst for the preparation of a homopolymer and/or copolymer having an irregular particle structure, which comprises reacting a Ti(IV) compound with an aluminum compound at from -40°C to 50°C in a molar ratio of from 1:0.01 to 1:4 for from 0.5 minute to 60 minutes.
8. The process for preparing a catalyst for the preparation of a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 7, wherein the aluminum component is added to a suspension medium in a ratio to the Ti component of Al:Ti = 1:1 - 30:1, preferably 2:1 to 20:1.
9. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 7 or 8, wherein the reaction of the Ti(IV) compound with the organic aluminum compound is carried out in a saturated hydrocarbon or a mixture of saturated hydrocarbons at a temperature of from -40°C to 100°C.
10. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 7 to 9, wherein the concentrations of the reactants in the starting solutions are from 0.1 mol to 9.1 mol of Ti(IV) compound/l of solvent and 0.01 mol to 1 mol of Al compound/l.

11. The process for preparing a catalyst for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 7 to 10, wherein the reaction of the components is carried out by adding the Ti(IV) component to the Al component over a period of from 0.1 minute to 60 minutes.
- 5

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PCT/EP99/07085

## Description

## Process for preparing a polymer

- 5 The present invention relates to a process for preparing a catalyst, a novel polymer and a process for preparing the polymer.

In processing of polyethylene, the polyethylene is usually melted and shaped to form a compact molding. From an economic point of view, the use of a polymer which is as compact as possible is always desirable. This objective becomes particularly clear in the preparation and use of ultrahigh molecular weight polyethylene. This is described in the prior art in JP-A-07041514, JP-A-06179720, EP-A-574153, JP-A-05070519.

- 15 Fillers are predominantly distributed homogeneously in the melt of the polymer. If this is impossible from a processing point of view, the use of polymer having an irregular structure is a possibility. The bulk density of the polymer can be employed as an easy-to-use physical measure of the particle and powder morphology. Thus, JP-A-519120423 describes the use of graphite-filled UHMWPE. The use of UHMWPE having a bulk density of less than 0.25 g/ccm is advantageous here.

- In addition, the processing of UHMWPE under reduced pressure to form porous semifinished and finished parts is known. For use as filter elements, a low pressure drop is necessary. Here too, an irregular structure of the sintered UHMWPE material is very helpful; cf. JP-A-09003236, JP-A-09001633.

- 30 In the production of filter elements, both requirements apply at the same time. EP-A-0 554 223 discloses a process for producing a filter unit. The morphology and low bulk density of the binder and the activated carbon are matched to one another. The high viscosity of the binder results in a lower strength of the resulting filter unit.

- 35 US-A-4,753,728 discloses an activated carbon filter block comprising activated carbon particles which are bound by a polymer to form a filter block. The polymer has a melt flow index of less than about 1 gram per 10

minutes, determined in accordance with ASTM D 1238 at 190°C and a loading of 15 kilograms. The polymer becomes sticky at elevated temperature. The polymer does not become sufficiently liquid to wet the activated carbon particles to a significant extent. A commercially available polymer GUR<sup>®</sup> 212 which has a melt flow index of < 0.1 gram per 10 minutes, determined in accordance with ASTM D 1238 at 190°C and a loading of 15 kilograms, and is an ultrahigh molecular weight polyethylene is disclosed.

10 EP-A-0 792 673 discloses a binder for producing filters by the extrusion technique. The binder has very high flow and an inhomogeneous distribution. The inhomogeneous distribution in the mixture leads to a fragile product. In addition, it comes to the surface of the activated carbon through the binder. The result is a decrease in the filter capacity.

15 Apart from the molar mass and the morphology, the particle size of the polymer also has to be matched to the filler to make homogeneous mixing possible and to reduce demixing during processing of the pulverulent mixtures.

20 The previously known processes for preparing polyethylene make it possible to influence the external shape of the polymer particles only within very narrow limits. The mean catalyst particle size is usually determined during the preparation of the catalyst. It is known that the catalyst particle size can be influenced in a targeted way by shearing during and after production of the solid catalyst particle by chemical reaction of the individual components. The particle size usually decreases at higher shear. At a circumferential velocity of the stirrer fixed by engineering circumstances, the shear can be controlled by varying the solvent viscosity. 25 If, in addition, the solvent is predetermined, its viscosity can be influenced by means of the temperature. As the temperature decreases, the shear generally increases owing to the higher viscosity of the solvent. This results in catalysts having a low particle size. Thus, the catalyst described in EP-A-0645403 is prepared at a low temperature in order to obtain a finely 30 particulate catalyst. The use of higher viscosity solvents in the preparation of the catalyst also leads to an analogous result.



It is an object of the present invention to provide an economical and environmentally friendly process for preparing a homopolymer and/or copolymer having an irregular particle structure.

This object is achieved by a process for preparing a homopolymer and/or copolymer having an irregular particle structure, which comprises polymerizing the monomers in the presence of a mixed catalyst comprising a titanium component and an organic aluminum compound and the presence of a molar mass regulator.

The process of the invention preferably gives a polyethylene having a viscometrically measured molar mass of  $1.5 - 4.1 \times 10^5$  g/mol (M by the Margolies method =  $5.37 \times 10^4$  [IV]<sup>1.49</sup>), a bulk density of less than 0.4 g/ccm, in particular from 0.05 g/ccm to 0.4 g/ccm, and a mean particle size of 5 – 300 µm and a molar mass distribution  $M_w/M_n$  of 3 – 30 or preferably a polyethylene homopolymer and/or copolymer having a melt flow index (MFR 190/15) of from 1.3 g/10 min to 10 g/10 min, a molecular weight distribution  $M_w/M_n$  of from 3 to 30, a bulk density of from 0.05 g/cc to 0.4 g/cc and a particle size of from 5 µm to 300 µm. A polyethylene homopolymer and/or copolymer having a melt flow index (MFR 190/15) of from 1.3 g/10 min to 10 g/10 min, a molecular weight distribution  $M_w/M_n$  of from 3 to 10, a bulk density of from 0.1 g/cc to 0.4 g/cc and a particle size of from 20 µm to 200 µm or a polyethylene homopolymer and/or copolymer having a melt flow index (MFR 190/15) of from 1.4 g/10 min to 5 g/10 min, a molecular weight distribution  $M_w/M_n$  of from 4 to 8, a bulk density of from 0.13 g/cc to 0.3 g/cc and a particle size of from 60 µm to 180 µm is particularly preferably obtained. A polyethylene homopolymer and/or copolymer having a melt flow index (MFR 190/15) of from 1.4 g/10 min to 3 g/10 min, a molecular weight distribution  $M_w/M_n$  of from 4 to 8, a bulk density of from 0.15 g/cc to 0.28 g/cc and a particle size of from 60 µm to 160 µm is very particularly preferably obtained.

The process of the invention makes it possible to prepare preferably pulverulent polyethylene having particle sizes which can be varied. The molar mass of the polymer should be set so that a material having a

measurable flow is obtained. At the same time, a narrow molar mass distribution ensures that the pores of the activated carbon are not blocked during sintering in filter production. Furthermore, sufficient powder flow should ensure good drying and conveying behavior.

5

In addition, variation of the polymer morphology is made possible. This can be achieved by means of the polymerization temperature selected or else by means of the ethylene partial pressure. Both a higher temperature and a higher ethylene partial pressure in the polymerization result in an increase in the bulk density.

10

The titanium component used according to the invention is obtained in a single-vessel reaction. The diluted Ti(IV) compound is reacted with the diluted aluminum compound at from  $-40^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  in a molar ratio of from 1:0.01 to 1:4 for from 0.5 minute to 60 minutes.

15

According to the invention, the particle size of the catalyst is determined by the activation temperature of the catalyst. This can influence the particle size of the polymer, which correlates with the particle size of the catalyst solid because of the replication behavior due to the multigrain behavior.

20

The reaction of the Ti(IV) compound with the organic aluminum compound is carried out in a pure saturated hydrocarbon or a mixture of saturated hydrocarbons at temperatures of from  $-40^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , preferably from  $-20^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ , particularly preferably from  $0^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ . The concentrations of the reactants in the starting solutions are from 0.1 mol to 9.1 mol of Ti(IV) compound/l of solvent and from 0.01 mol to 1 mol of Al compound/l, in particular from 0.2 mol to 5 mol of Ti(IV) compound and from 0.02 mol to 0.2 mol of Al compound.

25

30

To react the components, the Ti(IV) component is added to the Al component. The addition time is from 0.1 minute to 60 minutes, preferably from 1 minute to 30 minutes. Depending on the temperature, the reaction is complete after from 1 minute to 600 minutes. Cerimetrically, the Ti(III) yield is at least 95%.

35

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The polymerization is carried out in suspension in one or more stages, continuously or batchwise. The polymerization temperature is from 30°C to 130°C, preferably from 50°C to 90°C. The ethylene partial pressure is set in accordance with the bulk density required of the polymer. It is less than 5 4 MPa, in fact from 0.05 MPa to 4MPa, preferably from 0.02 MPa to 2 MPa, particularly preferably from 0.04 MPa to 1 MPa. As is customary in Ziegler-Natta polymerizations, an organoaluminum compound is used as cocatalyst. The aluminum component is added to the suspension medium in a ratio to the Ti component of Al:Ti = 1:1 - 30:1. The preferred Al:Ti ratio 10 is in the range from 2:1 to 20:1.

The reaction medium for the polymerization is, as is customary in Ziegler-Natta polymerizations, an inert solvent such as butane, pentane, hexane, cyclohexane, nonane, decane or their higher homologues and isomers as 15 pure substances or mixtures. The solvent is freed of catalyst poisons such as oxygen, moisture or sulfur compounds before use.

The molar masses of the polymers can be adjusted in a known manner by introduction of appropriate components. Preference is given to using 20 hydrogen. The ratio of ethylene partial pressure to hydrogen partial pressure is from 0.5:1 to 10:1, preferably from 2:1 to 8:1.

Addition of 1-olefins makes it possible, as is known, to obtain corresponding copolymers in addition to ethylene homopolymers. 25

The polymer is separated from the suspension medium under inert gas and dried in a fluidized bed. When using high-boiling hydrocarbons, the reaction product is subjected beforehand to treatment with steam.

30 The suspension medium is returned directly to the polymerization reactor.

Stabilizing additives such as the customary salts of long-chain fatty acids, e.g. calcium, zinc or magnesium stearate, can be added to the polymer.

35 To describe the polymers, the following values are reported:

mean particle diameter ( $d_{50}$ ): determined by laser light scattering using the particle size analyzer Helos-Rhodos measurement and data processing system from Sympatec GmbH, optical concentration = 4-7%,

- 5 bulk density (BD): determined in accordance with DIN 53 466,

melt flow index (MFR): the melt flow index 190/15 was determined in accordance with ISO 1133; 0.2% of ionol were added as stabilizer,

- 10 viscosity number (VN): determined in accordance with ISO 1628-3 in decalin at a concentration of 0.1 g/dl; to calculate the molar mass, the limiting viscosity (IV) is calculated therefrom using the Martin equation,

- B value: this value gives, as dimensionless parameter, information about the particle size of the catalyst. On the basis of the replication effect, the following relationship applies:  $\log(\text{catalyst yield}) = 3 \times \log(d_{50}) - B$ . The smaller the B value, the finer the mean particle diameter of the catalyst.
- 15

The invention is illustrated by the examples:

20

### Examples

#### Preparation of catalyst

- 25 13 mol of isoprenylaluminum (IPRA) and 252 l of Exxsol were placed under a protective gas blanket in a 600 l vessel. At an initial temperature of 8°C - 13°C, a solution of titanium tetrachloride in Exxsol® D30 (concentration: 3000 mmol/l) was added while stirring, so that a ratio of Ti:IPRA of 1:0.78 was established in the reaction mixture. The addition time
- 30 was 120 sec -- 140 sec. The reaction proceeded exothermically and spontaneously. The temperature rose quickly by 5°C over a period of 4 minutes. The mixture was stirred while cooling for 2 hours to allow further reaction to occur. After 15 hours, the upper phase was decanted off. The solid was admixed with 200 l of Exxsol® D30 and 0.7 mol of IPRA, and
- 35 then used for polymerization.

## Polymerization

The polymerization was carried out in one stage in a continuously operated plant with recirculation of the suspension medium. The suspension medium used was a mixture of saturated hydrocarbons having a boiling point range of 140°C – 170°C (Exxsol<sup>®</sup> D30) which had previously been purified over molecular sieves and aluminum oxide. The polymerization was carried out in a 40 l reactor at a reaction temperature of 70°C – 82°C and an ethylene partial pressure of from 0.16 MPa to 0.27 MPa.

On the basis of experience, the bulk density of the polymer increases by about 0.02 – 0.05 g/l on scale-up.

Examples 5 and 6 were carried out like Examples 1 to 4. In Examples 5 and the amount of catalyst used was reduced from 0.95 mmol of Ti/kg of PE to half this quantity. To be able to achieve the required product properties, both the reaction temperature and the ethylene partial pressure were increased compared to Examples 1 to 4.

The parameters and measurement results are shown in the table below.

Table

Activation temp. of the catalyst	Polymer -ization temp.	p(C <sub>2</sub> H <sub>4</sub> )	C <sub>2</sub> H <sub>4</sub> / H <sub>2</sub>	MFR 190/15	BD	d(50)	B value	Ex.
[°C]	[°C]	[bar]		[g/10min]	[g/l]	[µm]		
9	70	2.20	2.04	1.6	163	97	3.52	1
10	70	1.65	1.92	1.9	161	145	3.47	2
11	70	1.65	2.04	1.6	171	97	2.94	3
12	70	1.68	2.23	1.8	187	84	2.80	4
10	82	2.7	n.d.	1.4	190	172	3.41	5
13	80	2.4	n.d.	1.4	230	85	2.42	6

## Claims

1. A process for preparing a homopolymer and/or copolymer having an irregular particle structure and
 

a melt flow index (MFR 190/15)	of from 1.3 g/10 min to 10 g/10 min,
a molecular weight distribution $M_w/M_n$	of from 3 to 30,
a bulk density	of from 0.05 g/cc to 0.4 g/cc and
a particle size	of from 5 $\mu\text{m}$ to 300 $\mu\text{m}$ ,
- 5 by polymerization of the monomers using a mixed catalyst prepared by reacting a Ti(IV) compound with an organic aluminum compound at from 20°C to 50°C in a suspension medium for from 0.5 minute to 60 minutes.
- 10 2. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1, wherein
 

the melt flow index (MFR 190/15)	is from 1.3 g/10 min to 10 g/10 min,
the molecular weight distribution $M_w/M_n$	is from 3 to 10,
the bulk density	is from 0.1 g/cc to 0.4 g/cc and
the particle size	is from 20 $\mu\text{m}$ to 200 $\mu\text{m}$ .
3. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in claim 1 or 2, wherein
 

the melt flow index (MFR 190/15)	is from 1.4 g/10 min to 5 g/10 min,
the molecular weight distribution $M_w/M_n$	is from 4 to 8,
the bulk density	is from 0.13 g/cc to 0.3 g/cc and
the particle size	is from 60 $\mu\text{m}$ to 180 $\mu\text{m}$ .
- 15 4. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 3, wherein

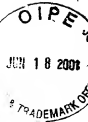
the melt flow index (MFR 190/15)	is from 1.4 g/10 min to 3 g/10 min,
the molecular weight distribution $M_w/M_n$	is from 4 to 8,
the bulk density	is from 0.15 g/cc to 0.28 g/cc and
the particle size	is from 60 $\mu\text{m}$ to 160 $\mu\text{m}$ .

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5. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 4, wherein the polymerization is carried out at a temperature of from 30°C to 130°C and a pressure of from 0.05 MPa to 4 MPa.
6. The process for preparing a homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 5, wherein the polymerization is carried out at a temperature of from 50°C to 90°C.
7. The process for preparing an ethylene homopolymer and/or copolymer having an irregular particle structure as claimed in one or more of claims 1 to 6, wherein the concentrations of the reactants in the starting solutions in the preparation of the mixed catalyst are from 0.1 mol to 9.1 mol of Ti(IV) compound/l of solvent and from 0.01 mol to 1 mol of Al compound/l.

### Process for preparing a polymer

- 5 The present invention relates to a process for preparing a catalyst, a novel polymer and a process for preparing the polymer. In particular, the invention provides a process for preparing a homopolymer and/or copolymer having an irregular particle structure and
- |   |  |
|---|--|
| a melt flow index (MFR 190/15)            | of from 1.3 g/10 min to 10 g/10 min,           |
| a molecular weight distribution $M_w/M_n$ | of from 3 to 30,                               |
| a bulk density                            | of from 0.05 g/cc to 0.4 g/cc and              |
| a particle size                           | of from 5 $\mu\text{m}$ to 300 $\mu\text{m}$ , |
- which comprises polymerizing the monomers in the presence of a mixed catalyst comprising a titanium component and an organic aluminum
- 10 compound and the presence of a molar mass regulator.





I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

In the matter of the above-identified application, please recognize Rudolf E. Hutz, Reg. No. 22,397; John D. Fairchild, Reg. No. 19,756; Harold Pezzner, Reg. No. 22,112; Richard M. Beck, Reg. No. 22,580; Paul E. Crawford, Reg. No. 24,397; Patricia Smink Rogowski, Reg. No. 33,791; Robert G. McMorrow, Jr., Reg. No. 30,962; Ashley I. Pezzner, Reg. No. 35,646; William E. McShane, Reg. No. 32,707; Mary W. Bourke, Reg. No. 30,982; Gerard M. O'Rourke, Reg. No. 39,794; James M. Olsen, Reg. No. 40,408; Francis DiGiovanni, Reg. No. 37,310; Eric J. Evain, Reg. No. 42,517; Daniel C. Mulveny, Reg. No. 45,897; Christine M. Hansen, Reg. No. 40,634; Patrick H. Higgins 39,709 and Elliot C. Mendelson (Agent), Reg. No. 42,878, all of P.O. Box 2207, Wilmington, Delaware 19899-2207 as attorneys with full power of substitution to prosecute this application and conduct all business in the Patent and Trademark Office connected therewith.

**CONNOLLY AND HUTZ**  
P.O.Box 2207  
Wilmington, Delaware 19899  
Telephone (302) 658-9141

INVENTOR(S) / Residence

1) Dr. Jens Ehlers, Krummer Weg 18, 46499 Hamminkeln, Germany *DEX*

Signature: 

Date: 05/03/2001

2) Dr. Stanislaw Hafka, Am Friedenshof 64, 46485 Wesel., Germany

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

3) Louis Wang, 1323 Chippenham Ct., 77459 Missouri City, Texas, USA

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

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P.O.Box 2207  
Wilmington, Delaware 19899  
Telephone (302) 658-9141

**INVENTOR(S) / Residence**

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Signature: \_\_\_\_\_ Date: \_\_\_\_\_

- 2) Dr. Stanislaw Haftka, Am Friedenshof 64, 46485 Wesel,, Germany

Signature:  \_\_\_\_\_ Date: 11.05.07

- 3) Louis Wang, 1323 Chippenham Ct., 77459 Missouri City, Texas, USA

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

06720-528/860



I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Wilmington, Delaware 19899  
Telephone (302) 658-9141

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Signature: \_\_\_\_\_ Date: \_\_\_\_\_

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Signature: \_\_\_\_\_ Date: \_\_\_\_\_

- 3) Louis Wang, 1323 Chippenham Ct., 77459 Missouri City, Texas, USA

Signature: Louis Wang Date: Mar. 10, 2001

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TIC 1998/G021 US PCT

The inventors are citizens of .

Post Office Address of all Inventors: Ticona GmbH  
Patent- und Lizenzabteilung  
D-60528 Frankfurt am Main  
Germany

1061/0.5/8/8/60

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:  
My residence, post office address and citizenship are as stated below next to my name.  
I believe I am the original, first and sole inventor (if only one name is listed below) or an  
original, first and joint inventor (if plural names are listed below) of the subject matter which  
is claimed and for which a patent is sought on the invention entitled

**Process for preparing a polymer**

the specification of which

(check one) is attached hereto.

was filed on September 23, 1999  
as International Patent Application PCT/EP99/07085

Application Serial No. 09/787,875 and

was amended on \_\_\_\_\_  
(if applicable)

was amended through \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above identified  
specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to  
patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 365(b) of any foreign  
application(s) for patent or inventor's certificate, or §365(a) of any PCT International  
application which designated at least one country other than the United States, listed below  
and have also identified below, by checking the box, any foreign application for patent or  
inventor's certificate, or PCT International application having a filing date before that of the  
application on which priority is claimed:

**Prior Foreign Application(s) for which Priority is Claimed:**

Federal Republic of Germany, 19843858.3 of September 25, 1998

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States  
application(s) listed below and, insofar as the subject matter of each of the claims of this  
application is not disclosed in the prior United States application in the manner provided by  
the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose  
to the Office all information known to me to be material to patentability as defined in Title 37,  
Code of Federal Regulations, § 1.56 which became available between the filing date of the  
prior application and the national or PCT international filing date of this application.

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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In the matter of the above-identified application, please recognize Rudolf E. Hutz, Reg. No. 22,397; John D. Fairchild, Reg. No. 19,756; Harold Pezzner, Reg. No. 22,112; Richard M. Beck, Reg. No. 22,580; Paul E. Crawford, Reg. No. 24,397; Patricia Smink Rogowski, Reg. No. 33,791; Robert G. McMorrow, Jr., Reg. No. 30,962; Ashley I. Pezzner, Reg. No. 35,646; William E. McShane, Reg. No. 32,707; Mary W. Bourke, Reg. No. 30,982; Gerard M. O'Rourke, Reg. No. 39,794; James M. Olsen, Reg. No. 40,408; Francis DiGiovanni, Reg. No. 37,310; Eric J. Evalin, Reg. No. 42,517; Daniel C. Mulveny, Reg. No. 45,897; Christine M. Hansen, Reg. No. 40,634; Patrick H. Higgins 39,709 and Elliot C. Mendelson (Agent), Reg. No. 42,878, all of P.O. Box 2207, Wilmington, Delaware 19899-2207 as attorneys with full power of substitution to prosecute this application and conduct all business in the Patent and Trademark Office connected therewith.

**CONNOLLY AND HUTZ**  
P.O. Box 2207  
Wilmington, Delaware 19899  
Telephone (302) 658-9141

**INVENTOR(S) / Residence**

- 1) Dr. Jens Ehlers, Krummer Weg 18, 46499 Hamminkeln, Germany

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

- 2) Dr. Stanislaw Haftka, Am Friedenshof 64, 46485 Wesel, Germany

Signature: Haftka Date: 11.05.01

- 3) Louis Wang, 1323 Chippenham Ct., 77459 Missouri City, Texas, USA

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

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**CONNOLLY AND HUTZ**  
**P.O.Box 2207**  
**Wilmington, Delaware 19899**  
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Signature: \_\_\_\_\_ Date: \_\_\_\_\_

- 3) Louis Wang, 1323 Chippenham Ct., 77459 Missouri City, Texas, USA

Signature: Louis Wang Date: Mar 10, 2001

The inventors are citizens of . 1-2) Germany; 3) USA

Post Office Address of all Inventors: Ticona GmbH  
Patent- und Lizenzabteilung  
D-60528 Frankfurt am Main  
Germany

09/87875.0/1901  
T06120'S/8/8/60





## COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:  
My residence, post office address and citizenship are as stated below next to my name.  
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

### Process for preparing a polymer

the specification of which

(check one) is attached hereto.

was filed on September 23, 1999  
as International Patent Application PCT/EP99/07085

Application Serial No. 09/787,875 and

was amended on \_\_\_\_\_  
(if applicable)

was amended through \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

### Prior Foreign Application(s) for which Priority is Claimed:

Federal Republic of Germany, 19843858.3 of September 25, 1998

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

006120-52828/60

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

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**CONNOLLY AND HUTZ**  
**P.O. Box 2207**  
**Wilmington, Delaware 19899**  
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8

INVENTOR(S) / Residence

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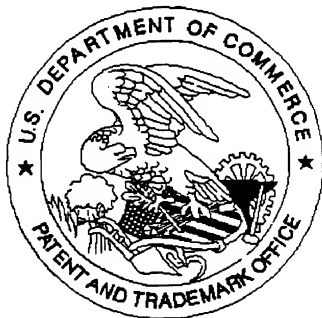
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